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**Vibration-Rotation Structure in Absorption Bands
For the Calibration of Spectrometers
From 2 to 16 Microns**



**U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS**

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Earle K. Plyler, Alfred Danti, L. R. Blaine, and E. D. Tidwell

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Earle K. Plyler, Alfred Danti,² L. R. Blaine, and E. D. Tidwell

(September 23, 1959)

Suitable bands of common gases have been tabulated and remeasured wherever necessary from 2 to 16 microns to obtain an accuracy of about 0.03 cm^{-1} throughout the region and to provide good calibrating points at frequent intervals. Some 600 rotation-vibration lines are illustrated in 20 spectrograms and wavenumbers are listed in companion tables with considerable intercomparison with worthy data obtained in other laboratories. The absorption bands were remeasured or calibrated by using either a precisely graduated grating circle or standard atomic lines with the fringe system formed by a Fabry-Perot interferometer. Characteristic features of the individual bands are discussed briefly and references to other publications are given. The substances used for calibration include H_2O , CO_2 , CO , HCl , HBr , NH_3 , C_2H_2 , CH_4 , N_2O , and polystyrene film.

1. Introduction

In recent years, infrared spectroscopists have expressed concern regarding satisfactory methods and wavelengths for calibrating good prism and small grating spectrometers [1, 2, 3, 4].³ In the past, a number of publications [5, 6, 7, 8, 9, 10, 11] from several laboratories did tend to ease the immediate requirements; but with the influx of finer instruments the need for more thorough, suitable, and precise coverage has arisen. Professor Mizushima and fellow workers have clearly indicated in their detailed measurements [12] that the small grating instruments are certainly capable of producing rather precise data. The present work addressed itself to the need for bringing together and remeasuring suitable bands of common gases in order to certify absolute accuracy to within several hundredths of a cm^{-1} throughout the region and to provide calibration points at frequent intervals.

2. Utility of the Molecular Band Method

Although in several cases (extremely precise measurements on CO [13, 14, 15] and HCN [16]) the use of molecular bands for calibration purposes is probably as good as the use of atomic lines, this method should not take preference over the use of atomic lines when precise measurement is being considered. However, when measurements good to several hundredths of a cm^{-1} are sufficient or in cases where other limiting factors enter, viz, broad bands, then this method may

offer a number of advantages. In the case of prism instruments, the use of appropriate atomic lines for calibration is rather limited to the visible and near infrared regions and the need for single order coverage throughout is apparent. Present day commercial instruments are more easily calibrated in absorption than in emission and the molecular band method obviates the need for a full battery of atomic line equipment as well as personnel capable of using it. In addition, only available or easily obtainable substances have been used in this work so that laboratories should experience little difficulty in using this method. Most of the gases are available in typical chemistry laboratories and it will be mentioned that work in this laboratory has indicated that, in general, natural gas from commercial lines and acetylene drawn from the welder's tank are suitable for calibration purposes. Should impurity peaks arise in these bands, use can still be made of the lines which are clearly those tabulated and illustrated in the following sections.

Some 600 lines, which provide rather thorough coverage, are tabulated and illustrated in 20 spectrograms. For certain bands, the number can be appropriately increased by having reference to recommended publications given in the discussion section. Attempts were made to keep the number of different gases used at a minimum and they include: H_2O , CO_2 , CO , HCl , HBr , NH_3 , C_2H_2 , CH_4 , and N_2O . Also a polystyrene film has been included.

3. Instruments and Methods Used in Calibrating the Standard Lines

Two instruments in the Radiometry Section of the NBS were used in measuring the bands and in the 2- to $4\text{-}\mu$ region most bands were measured on both instruments at different resolution and the results compared.

¹ This research was supported by the Air Force Cambridge Research Center and by a NASF grant to MIT.

² Guest worker from MIT.

³ Figures in brackets indicate the literature references at the end of this paper.

3.1. 5 to 16 Micron Region

a. Instrument

The previously described [17] grating spectrometer with an off-axis collimating mirror of 1-m focal length was used in conjunction with an extremely precise grating circle reported to be accurate to at least 3 sec of arc for any angle [18]. For the longer wave work (5 to 16 μ) the lead telluride detector was replaced with a thermocouple detector. When this instrument was used in the 2- to 4- μ region, the thermocouple detector was purposefully used so that resolution could be lowered and made comparable to that of small grating instruments. A KBr foreprism arrangement with fixed foreprism slits and a manually adjustable prism was used for order separation throughout this work. Under these stated conditions the instrument was capable of resolving lines separated by 0.3 cm^{-1} in the 7- to 16- μ region and up to about 1 cm^{-1} in the 2.5- to 6.5- μ region.

b. Method of Calibration

With a microscope attachment, angles were read off the inscribed circle, centered with respect to the spindle of the cone which rotates the grating, and fiducial marks recorded on the chart. During measuring runs, readings were taken every 5 min of arc and a slow drive speed (~ 23 min per deg) was used. It was found that proper positioning of the foreprism energy upon the entrance slit of the spectrometer proper was necessary in the sense that for extreme settings, where the maximum of energy being admitted to the spectrometer would come about 5 grating degrees away from the point of interest, the frequencies of measured lines would be in error by several hundredths of a cm^{-1} . By making frequent settings of the foreprism (about every 2 deg of grating angle) so that the energy would be maximized and hence placed symmetrically on the entrance slit, these effects could be ignored. Such considerations were, of course, of greater importance in regions where wide spectrometer slits were required or at long wavelengths where the dispersion of KBr is greatest. (This matter was considered in some detail, since it is felt that it is a frequently overlooked source of error occurring with the use of foreprisms.) In the course of any complete run (standards plus spectrum to be measured) no changes were made in instrumental conditions (viz, retardation resulting from changes in amplifier response settings may shift the line center) unless absolutely necessary.

At the start of the work, it was decided that the precisely measured CO fundamental lines (see ref. [13]) (table 4) be used as standards wherever possible. The procedure devised was that of using the simplified grating relation, $n\lambda = K \sin \theta$, where an "effective" grating constant, K_{air} , incorporating spectrometer characteristics, could be calculated by measuring about 15 CO lines and the physical central image. This was done with the grating being turned first in one direction then in the reverse direction. If slightly different, the K 's obtained separately for each direction would be averaged. Once a good

value of K had been determined for a grating, the central image was always calculated from the 10 (or so) standard lines recorded either before or immediately following a measuring run. Using this procedure, the frequency of standard CO lines could always be recalculated from chart measurements to within about $\pm 0.01 \text{ cm}^{-1}$ of the accepted value. With good spectrometer and grating alignment, it was felt that CO standards could be used to calibrate NH_3 , CH_4 , and H_2O lines even though the grating angle for the standards differed appreciably from that of the lines in question. In calibrating the lines, both standards and runs to be measured would be recorded with the grating being turned in the same direction. As is often the case, it was found that slightly different values would be obtained for the two directions. Final values represented the average of an equal number of measurements in each direction. It is believed that the tabulated values are accurate to $\pm 0.02 \text{ cm}^{-1}$ in this region.

c. Chart Reduction

Wherever possible single lines were picked out for measuring, but in some instances certain complex lines were measured since they are particularly suited for direct prism observation. It is advisable to record spectra on ruled chart paper where the ruled lines are reproducible perpendicular to the chart edge. The determined center point of the line to be measured can then be easily projected to a suitable measuring base line on the chart by using a pair of dividers and the nearest ruled line. The center of the line should be determined with a pair of stiff dividers at about the 2/3 absorption point and not at the peak or apparent maximum of absorption. If the spectrum is particularly noisy the center should be determined at a number of places from the 2/3 to 3/4 point of the maximum of absorption and the average taken. Fractional distances between "pip" marks should be measured to within 0.005 in. using a steel rule and visual enlarger if necessary. For the majority of measuring runs, 5 min of grating arc corresponded to 2 in. on the chart.

d. Instrument and Calibration

The instrument, which uses the double-pass system and is capable of resolving about 0.03 cm^{-1} has been described [19] and only a few details need be added. Standard atomic lines and the fringe system described in a previous paper (see ref. [17]) were used to calibrate the molecular bands. By scanning the spectrum slowly and averaging several runs, a set of relative values for the lines of a band can be determined to a few thousandths of a cm^{-1} and the absolute to $\pm 0.01 \text{ cm}^{-1}$. With scanning at a medium rate, absolute values are probably in error by $\pm 0.03 \text{ cm}^{-1}$. The accuracy of measurement of this instrument is increased by the lines being very narrow (0.03 cm^{-1}). Measurements made under lower resolution (about 1 cm^{-1}) with the other instrument in this region agreed with these to about $\pm 0.05 \text{ cm}^{-1}$. This indicates that low resolution

pectrometers can measure with an error of about 1/10 of the resolution.

e. Refractive Index

In this laboratory measurements on both instruments are carried out with the grating in air so that reported frequencies were corrected to vacuum by using refractive index tables, and temperature and pressure corrections given by Penndorf [20].

4. Comments on Measuring Technique and Use of the Standard Lines

For the present-day molecular spectroscopist who wishes to carry out precise measurements, useful points on measurement technique, whether on standard or unknown lines, have already been mentioned in previous sections on method of calibration, instrument performance, chart reduction, and also in reference [17]. Concerning a spectrum to be measured, in cases where the instrument is being used at or near its resolution limit (ripple spectrum) or in the case of complex lines or shoulders, then the best possible "center" point must be picked and this may necessarily have to be near the absorption peak since lines may not be well enough developed to permit measurement at the 2/3 to 3/4 absorption point.

It is advisable to record both spectra and standards for each direction of grating turn if the driving mechanism is equally accurate in both directions. Provisions or modifications should be made on commercial or laboratory instruments so that the grating can be used in both directions with near equal accuracy and the results averaged. Undoubtedly, in most laboratories the standards will be used in conjunction with reproducible pip marks. Data will be extracted from simple pip or drum number versus frequency (cm^{-1}) relations by fitting a straight line to two end points and an extended deviation curve plotted. In view of extremely precise data for certain bands (CO, HCN) the utility of using these standard lines in higher orders for the same grating angle should not be overlooked. In terms of precision measurement, it would appear that the ν_2 branch (1,000 to 1,200 cm^{-1}) of the ν_2 NH_3 band might also be classified in this category. This higher order procedure, of course, requires refractive index considerations for conversion to vacuum and each spectral region must be handled independently.

In making use of the standard lines under lower or higher resolution, workers should exercise necessary care. For example, in the CO bands where apart from some isotopic overlap) the lines are single and suitably spaced throughout, even ripple peaks observed with a prism instrument would serve as satisfactory calibration points. Whereas, in many other bands proper usage under lower resolution may require judicious use of sufficiently low pressures and slow scanning speeds to assure the proper development of lines and eliminate "pulling" by strong neighboring absorption.

5. Discussion of Spectrograms

In general, the runs made on white chart paper for illustration purposes were made at somewhat faster speeds and with much more chart concentration than was the case for the measuring runs. On some of the illustrations, sloping or bowing backgrounds are due either to foreprism effects or the joining of separate sections.

5.1. CO_2 , ν_2 Fundamental

Some 20 lines in this band were remeasured and comparison is made with the work of Rossman, Rao, and Nielsen [21-A, 21-B] and also with the values reported by Mizushima et al. (see ref. [12]). Although our measurements were somewhat handicapped by the overly strong absorption (7-m path) and also by poorer grating resolution in this region, the agreement is quite good. It appears that the values reported by Rossman, Rao, and Nielsen (also additional unpublished work communicated by Dr. Rao) are accurate and that lines they report both at higher and lower frequency as well as those given in table 1 may be used for calibration purposes provided the atmospheric absorption is augmented by CO_2 used in a vapor cell. The spectrum is illustrated in figure 1.

TABLE 1. Absorption lines of ν_2 fundamental of CO_2 from 635 to 700 cm^{-1}

J	R(J)			P(J)		
	Rossman, Rao, and Nielsen ^a $\nu \text{ cm}^{-1}$ (vac.) observed	This work $\nu \text{ cm}^{-1}$ (vac.) observed	Mizushima et al. ^b $\nu \text{ cm}^{-1}$ (vac.) observed	Rossman, Rao, and Nielsen ^a $\nu \text{ cm}^{-1}$ (vac.) observed	This work $\nu \text{ cm}^{-1}$ (vac.) observed	Mizushima et al. ^b $\nu \text{ cm}^{-1}$ (vac.) observed
2-----	669.75	-----	-----	665.83	-----	-----
4-----	71.34	-----	.28	64.28	-----	-----
6-----	72.88	.88	.87	62.71	-----	-----
8-----	74.45	.46	.43	61.18	.15	.15
10-----	76.02	.06	.02	59.64	.55	.60
12-----	77.60	-----	.59	58.08	.06	.09
14-----	79.20	-----	.16	56.55	.51	.53
16-----	80.78	-----	.76	55.02	4.98	.00
18-----	82.36	.39	.35	53.48	.48	.47
20-----	83.95	.98	.95	51.95	.91	.94
22-----	85.55	.56	.55	50.41	.39	.41
24-----	87.16	.17	.14	48.90	-----	.89
26-----	88.77	.79	.78	47.39	-----	.38
28-----	90.38	.36	.36	45.90	.89	.87
30-----	91.99	.97	.99	44.37	-----	.39
32-----	93.59	-----	.60	42.86	-----	.88
34-----	95.19	-----	.20	41.35	.40	.38
36-----	96.82	-----	.82	39.83	-----	.90
38-----	98.44	-----	.42	38.34	-----	.35
40-----	700.07	-----	.04	36.87	-----	.89
42-----	01.69	-----	.68	35.38	-----	.40
Q Branch..	^c (10°0'→01°0')	720.46	-----	-----	-----	-----

^a Rossman, Rao, and Nielsen [21].

^b Mizushima et al. [12].

^c The measuring point of this band was taken at the 2/3 absorption point.

5.2. Acetylene, ν_5 Fundamental

This band was included in order to provide useful calibration points between the end of the strong 15- μ CO_2 band and the ammonia band. On the low-

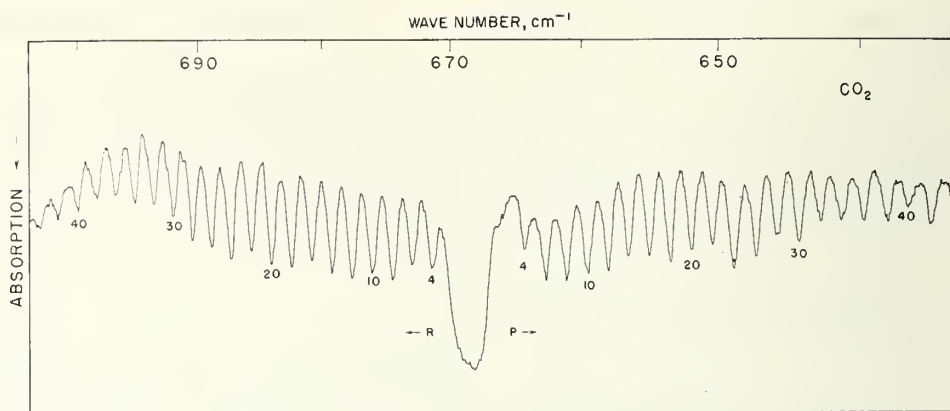


FIGURE 1. The ν_2 fundamental of CO_2 recorded in the first order of an 1,800 lines/in. grating under atmospheric conditions and 7-m path.
Spectral slit width about 0.5 cm^{-1} .

frequency end, our values are in excellent agreement with the recently published values of Rao, Ryan, and Nielsen [22] and table 2 includes additional values as reported by these authors. At higher frequency, results are also compared with the work of Christensen, Eaton, Green, and Thompson [23]. The agreement is quite good except between lines 29 to 39, where several lines appear to be pulled out of position by an overlapping band. These lines are set out by parentheses. Results of recent measurements by Jones and Nadeau of the National Research Council, Ottawa, Canada are also included. The spectrogram is illustrated in figure 2.

5.3. NH_3 , ν_2 Fundamental

Table 3 gives values obtained in four different laboratories for this band. Since these four works are of about equal quality, the average value reported in the last column represents a simple numerical average (within arbitrary $\pm 0.04\text{-cm}^{-1}$ exclusion conditions). The average values are probably better than individual determinations, and it is estimated that they are good to within $\pm 0.01\text{-cm}^{-1}$ absolute on the average. The region from 1,000 to $1,200 \text{ cm}^{-1}$ is particularly good. We have cause for suspicioning some of our low-frequency lines (numbers 1, 3, and 6) due to the fact that the grating was being used at exceedingly high angle. As more experimental and theoretical data become available for ammonia, a good set of calculated values may ultimately replace the average value column. The spectrum is shown in figure 3.

5.4. Methane, ν_4 Fundamental

This band serves the purpose of providing connection between the ammonia and water bands and is included mainly because workers with small instruments may have difficulty in observing weak water lines in this region. We are unable to compare these

TABLE 2. Absorption lines of ν_3 fundamental of acetylene from 680 to 790 cm^{-1}

Line serial number	This work $\nu \text{ cm}^{-1}$ (vac.) observed	Rao, Ryan, and Nielsen ^a $\nu \text{ cm}^{-1}$ (vac.) observed	C., E., G., and T ^b $\nu \text{ cm}^{-1}$ (vac.) observed	Jones and Nadeau ^c $\nu \text{ cm}^{-1}$ (vac.) observed
1	-----	686.77	-----	686.
2	-----	89.11	-----	89.
3	-----	91.47	-----	91.
4	-----	93.80	-----	93.
5	-----	95.19	-----	96.
6	698.53	98.52	698.50	98.
7	-----	700.89	700.88	700.
8	703.28	03.24	03.19	03.
9	^d (05.66)	05.60	05.56	05.
10	07.96	07.95	07.94	07.
11	10.30	10.30	10.37	10.
12	12.68	-----	12.67	12.
13	15.08	-----	15.03	15.
14	16.36	-----	-----	-----
15	17.35	-----	17.35	17.
16	19.90 (peak)	-----	19.90	19.
17	(22.15)	-----	22.06	21.
18	24.39	-----	24.35	-----
19	36.17	-----	36.18	36.
20	38.56	-----	38.56	38.
21	40.89	-----	40.88	40.
22	43.29	-----	43.31	43.
23	45.64	-----	45.64	45.
24	47.97	-----	48.02	47.
25	50.36	-----	50.37	50.
26	52.66	-----	52.74	52.
27	(55.12)	-----	55.14	55.
28	57.42	-----	57.45	57.
29	(59.85)	-----	59.86	59.
30	62.11	-----	62.18	62.
31	(64.46)	-----	64.52	64.
32	66.74	-----	66.87	66.
33	69.08	-----	69.21	69.
34	71.39	-----	71.53	71.
35	73.71	-----	73.84	73.
36	(76.02)	-----	76.17	76.
37	78.42	-----	78.52	78.
38	(80.70)	-----	80.82	80.
39	83.07	-----	83.09	83.
40	85.43	-----	85.45	85.
41	87.75	-----	87.74	-----
42	90.10	-----	90.12	-----

^a Rao, Ryan, and Nielsen [22].

^b Christensen, Eaton, Green, and Thompson [23].

^c Jones and Nadeau, National Research Council, Ottawa, Canada, unpublished work.

^d Parentheses around values in second column indicate poorer lines.

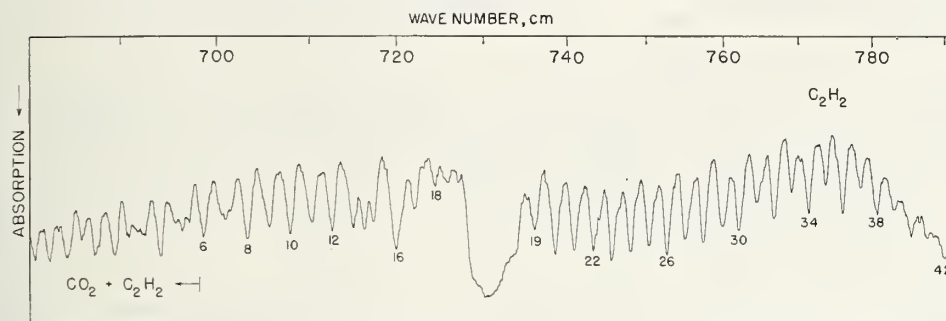


FIGURE 2. The ν_5 fundamental of acetylene recorded in the first order of an 1,800 lines/in. grating with 8-cm pressure and 5-cm path.

Spectral slit width about 0.7 cm^{-1} . The low frequency end of the P branch overlaps with atmospheric absorption of CO_2 and the strong Q branch (hot band) of CO_2 at 720.46 cm^{-1} also contributes to absorption at this point.

TABLE 3. Absorption lines of ν_2 fundamental of NH_3 from 760 to 1,210 cm^{-1}

Line Serial number	This work ν cm^{-1} (vac.) observed	Garing and Nielsen ^a ν cm^{-1} (vac.) observed	Price and coworkers ^b ν cm^{-1} (vac.) observed	Mizushima et al. ^c ν cm^{-1} (vac.) observed	Average value ^d ν cm^{-1} (vac.)
1	760.72	.69	.69	-----	.70
2	70.96	.91	.90	.96	.93
3	78.33	.29	.27	.33	.30
4	91.76	.72	.76	.75	.75
5	96.17	.14	.16	.15	.16
6	809.76	.72	.71	.74	.73
7	14.27	.25	.22	.24	.24
8	30.68	.65	.70	.67	.68
9	34.86	.82	.84	.83	.84
10	51.36	.32	.36	.32	.34
11	52.77	.71	.76	.73	.74
12	67.83 (blend)	(.53, .74, .93)	(.53, .73, .96)	.82	.82
13	71.77	.73	.74	.79	.76
14	72.59	.56	.58	.58	.58
15	87.99	.99	8.02	.96	.99
16	92.06 (blend)	(1.88, .14)	(1.88, .14)	.10	.08
17	908.21	.17	.15	.24	.18
18	18.65	.62	.61	-----	.63
19	35.85 (poor)	.90	.90	-----	.88
20	48.25	.22	.25	.27	.25
21	51.83	.77	.80	-----	.80
22	61.01 (poor)	.06	(0.89, .12)	-----	-----
23	71.91	.89	.92	.90	.90
24	91.71	.68	.71	-----	.70
25	92.60 (blend)	(.45, .70)	(.46, .71)	.64	.62
26	1,007.55	.54	.56	.48	.55
27	11.20	.20	.22	.24	.22
28	27.04	.04	.04	6.92	.04
29	32.14	.13	.13	.12	.13
30	46.41	.40	.42	.27	.41
31	53.14	.13	.14	.14	.14
32	65.58	.57	.55	.46	.57
33	70.60	.59	.59	.53	.59
34	74.17	.14	.17	.13	.15
35	84.61	.60	.62	.56	.61
36	89.38	.42	.39	.31	.40
37	95.15	.15	.16	.15	.15
38	1,103.44	.46	.42	.44	.44
39	10.67	.69	.69	.67	.68
40	16.02	.03	.03	5.97	.03
41	22.15	.14	.13	.10	.14
42	31.85	.86	.89	-----	.87
43	36.78	.76	.75	-----	.76
44	40.62	.65	.65	.58	.64
45	47.53	.52	.54	-----	.53
46	52.86	.86	.87	-----	.86
47	58.93	.98	.95	.90	.95
48	77.09	.08	.10	-----	.09
49	95.02	.00	4.99	-----	5.00
50	1,212.66	.68	.69	-----	.68

^a Garing, Nielsen, and Rao [24].

^b Price and coworkers [33].

^c Mizushima et al. [12].

^d Numerical average of the 4 determinations. If a number differed by 0.04 cm^{-1} or more from the average of the other 3, it was excluded from the average.

numbers with others, as there are no other precision measurements available but our results (see table 4) would appear to be good to about $\pm 0.02\text{-cm}^{-1}$ absolute. The spectrum is shown in figure 4.

5.5. H_2O , ν_2 Fundamental

Some 50 good lines of varying intensity were picked out for measurement. (See table 5.) Wherever possible, the lines are compared with recent precision determinations of Rao, Ryan, and Nielsen (see ref. [22]). These authors indicate that their values are, on the average, about 0.07-cm^{-1} lower than those reported by Dalby and Nielsen [25] for the region 1,450 to 1,650 cm^{-1} . Our results, when compared with Dalby and Nielsen's values, would indicate that this is the case throughout the band. Wherever possible, mild flushing or pumping down of the spectrometer housing is to be recommended for cleaner development of the lines but our results indicate that good calibration measurements can be made even on saturated lines provided the line is not a complex one. This band is illustrated in figure 5.

TABLE 4. Substructure of ν_1 band of CH_4 from 1,200 to 1,370 cm^{-1}

Serial number	This work ν cm^{-1} (vac.) observed
1	1,216.26
2	30.12
3	33.47
4	41.01
5	47.81
6	56.60
7	65.52
8	75.20
9	81.59
10	92.61
11	97.63
12	1,311.42
13	22.09
14	27.20
15	32.41
16	41.79
17	46.70
18	53.06
19	66.04

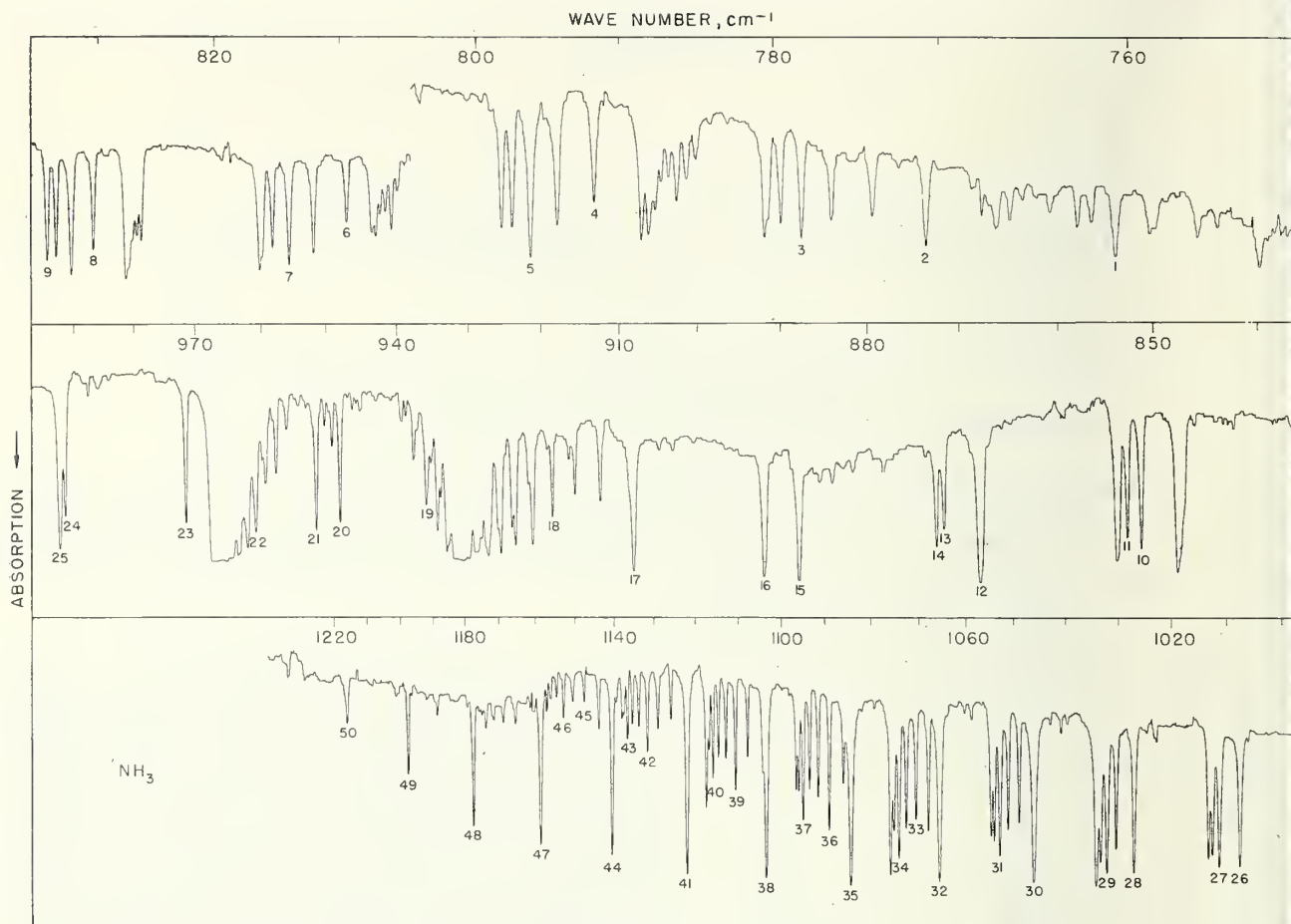


FIGURE 3. The ν_2 fundamental of NH_3 recorded in the first order of a 3,600 lines/in. grating with 7-cm pressure near the bar center and 12-cm for the wings, both with 5-cm path.

Spectral slit width about 0.3 cm^{-1} .

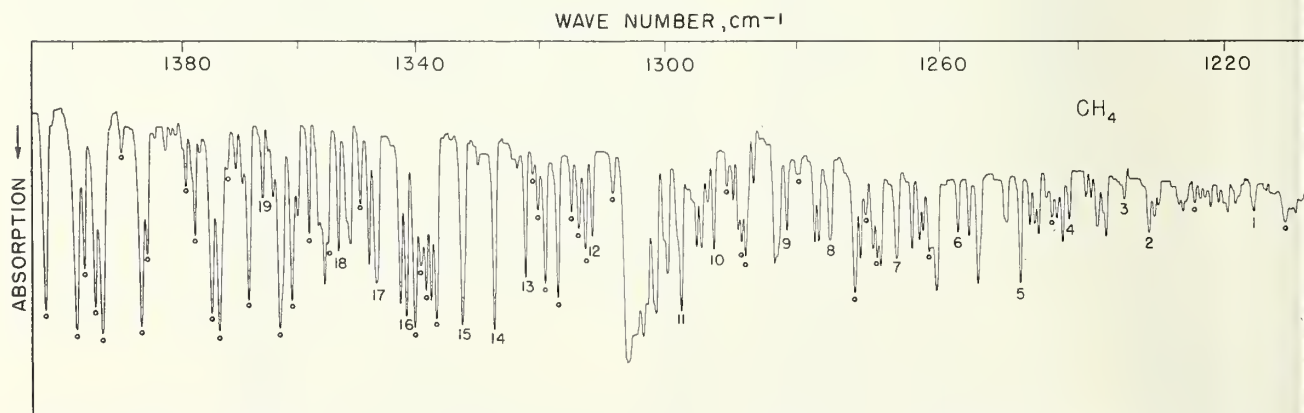


FIGURE 4. The ν_4 fundamental of CH_4 recorded in the first order of a 3,600 lines/in. grating with 12-cm pressure and 5-cm path.

Spectral slit width about 0.5 cm^{-1} . The open circles refer to atmospheric water peaks.

TABLE 5. Absorption lines of ν_2 fundamental of H_2O from 1,300 to 2,000 cm^{-1}

Line serial number	This work ν cm^{-1} (vac.) observed	Rao, Ryan, and Nielsen ^a ν cm^{-1} (vac.) observed	Line serial number	This work ν cm^{-1} (vac.) observed	Rao, Ryan, and Nielsen ^a ν cm^{-1} (vac.) observed
1	1,312.55	-----	26	16.77	16.72
2	18.92	-----	27	27.88	-----
3	36.68	-----	28	37.53	-----
4	54.83	-----	29	40.31	-----
5	61.08	-----	30	62.82	-----
6	68.62	-----	31	71.49	-----
7	75.07	-----	32	90.15	-----
8	94.46	-----	33	1,704.49	-----
9	1,404.99	-----	34	10.23	-----
10	17.42	-----	35	23.49	-----
11	29.94	-----	36	56.81	-----
12	47.93	-----	37	68.17	-----
13	52.04	-----	38	75.64	-----
14	64.92	64.91	39	84.95	-----
15	81.25	-----	40	^b (90.94)	-----
16	87.29	-----	41	99.60	-----
17	98.80	-----	42	1,810.63	-----
18	1,512.30	-----	43	25.24	-----
19	28.57	-----	44	47.80	-----
20	^b (45.09)	-----	45	69.35	-----
21	64.93	64.91	46	89.59	-----
22	94.52	94.51	47	95.19	-----
23	96.29	96.27	48	1,918.05	-----
24	1,601.25	01.23	49	42.60	-----
25	09.46	-----	50	88.43	-----
			51	^b (2,016.79)	-----

^a Rao, Ryan, and Nielsen [22].
^b These lines are less accurate.

5.6. CO Fundamental

The CO fundamental band at 4.67μ was measured accurately by Plyler, Blaine, and Connor (see ref. [13]) in 1955. With the measurement of the CO harmonic (2.33μ), it was possible to calculate the position of the fundamental band. This has been done by Rank and his colleagues (see ref. [14]) and a very good agreement with the observed values was obtained. There was a slight difference in values for the high J 's in the R branch. Recently the R branch has been re-measured and a better correspondence with the calculated values is obtained. The accuracy of the calculated values approaches a few thousandths of a cm^{-1} . The spectrum is shown in figure 6 and the values are listed in table 6.

5.7. C^{13}O_2 , ν_3 Fundamental

The C^{13}O_2 band is excellent for calibration from 2,240 to 2,280 cm^{-1} and connects with the ν_3 band of C^{12}O_2 . This spectrum was measured in 1955 by Plyler, Blaine, and Tidwell [26]. In this work, the lines of this band have been remeasured and the values check closely with the first determination. Unfortunately, the J values were incorrectly listed in table 1 of the above publication and each J of the P branch should be reduced by 2; that is, P 44 should

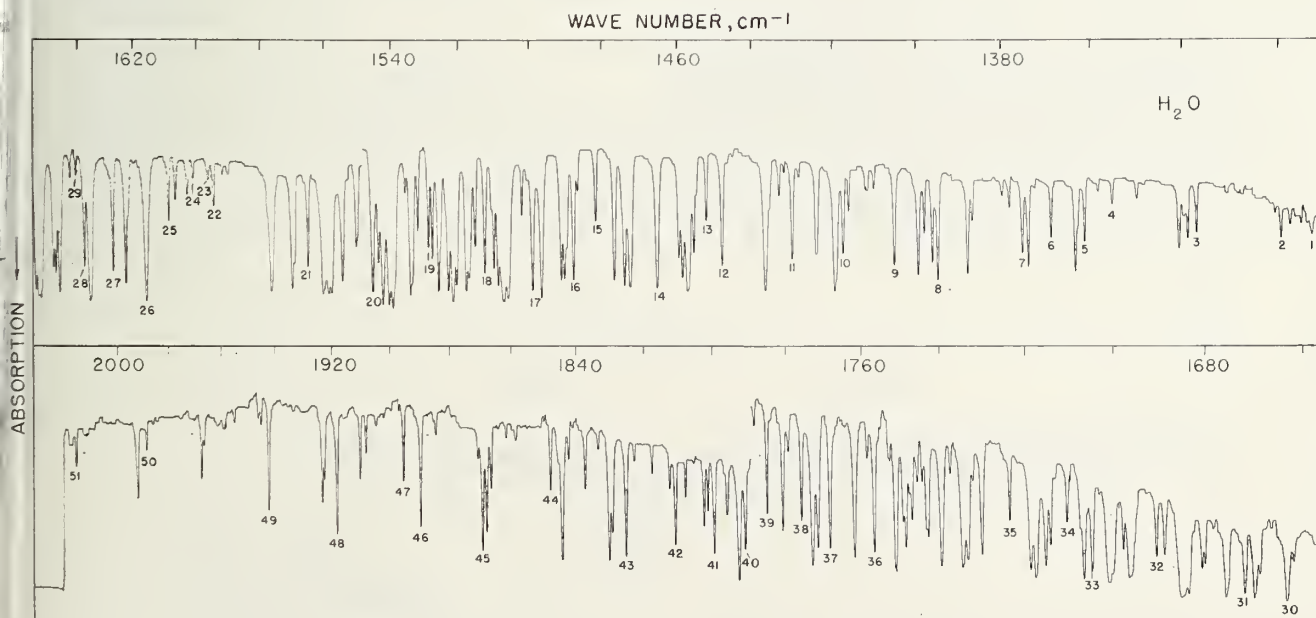


FIGURE 5. The ν_2 fundamental of H_2O recorded with a 3,600 lines/in. grating under atmospheric conditions ($T=21^\circ \text{C}$, humidity 21%) and 7-m path.

The upper spectrogram was recorded in the first order and the lower in the second order. Spectral slit width about 0.6 to 0.7 cm^{-1} for both spectrograms.

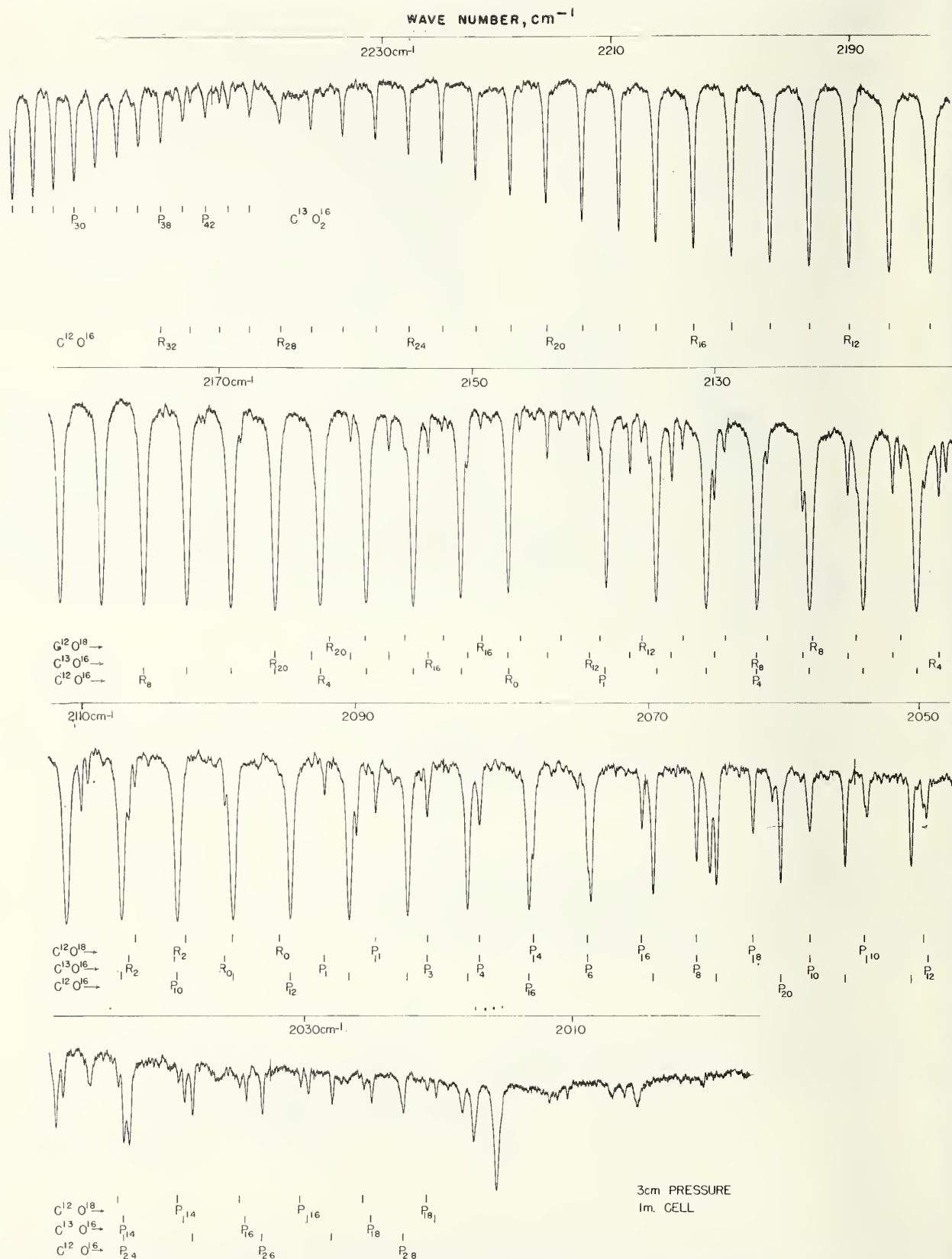


FIGURE 6. Absorption band of CO recorded in the first order of a 7,500 lines/in. grating with 3-cm pressure and 1-m path. Spectral slit width about 0.3 cm^{-1} .

TABLE 6. Absorption lines of CO from 2,020 to 2,240 cm^{-1}

Line number	Plyler, Blaine, and Connor ^a ν cm^{-1} (vac.) observed	Rank et al. ^b ν cm^{-1} (vac.) calculated	Line number	Plyler, Blaine, and Connor ^a ν cm^{-1} (vac.) observed	Rank et al. ^b ν cm^{-1} (vac.) calculated
P 28	2,022.899	.915	R 0	-----	-----
27	27.635	.650	1	-----	-----
26	32.349	.354	2	2,154.596	.598
25	37.030	.026	3	58.309	.302
24	41.663	.668	4	-----	-----
23	46.271	.278	5	65.602	.604
22	-----	-----	6	-----	-----
21	55.391	.402	7	72.759	.761
20	59.911	.916	8	76.287	.286
19	-----	-----	9	79.761	.774
18	68.851	.849	10	83.226	.226
17	-----	-----	11	86.636	.641
16	77.650	.652	12	90.010	.020
15	82.009	.005	13	93.357	.361
14	86.322	.324	14	96.661	.665
13	90.603	.611	15	99.929	.933
12	94.870	.855	16	2,203.147	.163
11	99.096	.085	17	06.345	.355
10	2,103.265	.272	18	09.498	.510
9	07.413	.426	19	12.600	.626
8	11.555	.546	20	15.685	.705
7	-----	-----	21	18.733	.746
6	19.677	.684	22	21.732 ^c 21.750	.749
5	23.700	.702	23	24.694	.713
4	-----	-----	24	27.638	-----
3	31.639	.635	25	30.526	-----
2	35.554	.549	26	33.362	-----
1	39.432	.429	27	36.186	-----
			28	38.958	-----

^a Plyler, Blaine, and Connor [13].^b Rank et al. [14].^c New measurements agreeing more closely with calculated values.TABLE 7-A. Absorption lines of ν_3 fundamental of $\text{C}^{13}\text{O}_2^{16}$ from 2,240 to 2,300 cm^{-1}

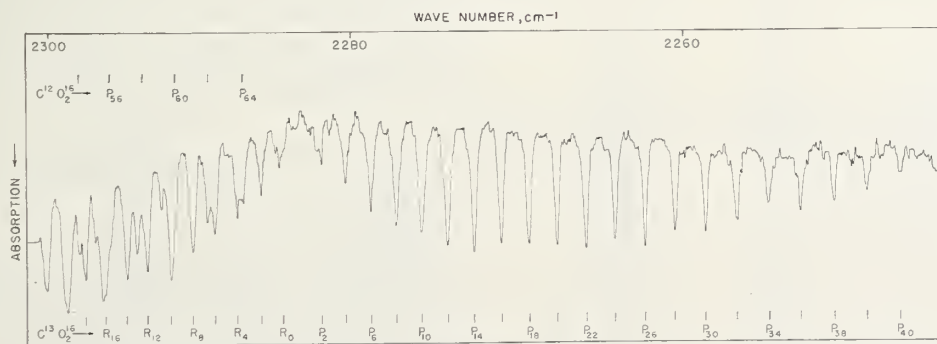
Line number	This work ν cm^{-1} (vac.) observed	Previous work Plyler, Blaine, and Tidwell ^a ν cm^{-1} (vac.) observed	Mizushima et al. ^b ν cm^{-1} (vac.) observed	Line number	This work ν cm^{-1} (vac.) observed	Previous work this laboratory ^c ν cm^{-1} (vac.) observed	Mizushima et al. ^b ν cm^{-1} (vac.) observed
P 40	2,247.68	2,247.66	-----	R 0	2,284.24	-----	-----
38	49.68	.68	-----	2	85.79	.76	.83
36	51.70	.67	-----	4	87.31	.33	.34
34	53.66	-----	-----	6	88.81	.80	.83
32	55.59	-----	-----	8	90.23	.20	.29
				10	91.62	.62	.73
30	57.52	.52	2,257.48	12	93.10	.12	-----
28	59.41	.42	.40	14	94.45	.46	-----
26	61.29	.30	.35	16	95.89	-----	.91
24	63.13	.14	.30	18	97.18	.20	.26
22	64.95	.96	5.04	20	98.50	-----	.57
				22	99.76	.74	-----
20	66.75	.76	.85	24	2,301.05	.06	-----
18	68.54	.55	.65				
16	70.29	.31	.37				
14	72.03	-----	-----				
12	73.73	.74	.73				
10	75.42	-----	-----				
8	77.09	.08	.03				
6	78.71	.71	.64				
4	80.33	.31	.18				
2	81.94	-----	-----				

^a Plyler, Blaine, and Tidwell [26].^b Mizushima et al. [12].^c E. K. Plyler and L. R. Blaine, unpublished work.

possible to measure the central part of the band. Figure 7-B shows how use can be made of the entire band by purging the instrument housing and containing the CO_2 in a cell. (Dr. Norman Jones of the National Research Council of Canada has furnished the spectogram as observed with a purged small grating instrument.) Table 7-B gives observed values for the band wings and calculated values for the central part. In view of the fact that molecular constants calculated from the observed lines agree well with those of Courtoy [27] obtained from many bands and agreement with observed lines is good, it is felt that workers can use either the observed or calculated values of table 7-B equally well provided the intensity and resolution of the band is close to that of figure 7-B. Both

5.8. C^{12}O_2 , ν_3 Band

The only precision work for this band is the work which was done at the NBS. The frequencies were first published in 1955 (see ref. [26]) and since then two other determinations have been made. With the long paths employed in this laboratory, it is not

FIGURE 7-A. The ν_3 fundamental of $\text{C}^{13}\text{O}_2^{16}$ recorded in the first order of a 7,500 lines/in. grating under atmospheric conditions and 6-m. path.Spectral slit width about 0.3 cm^{-1} .

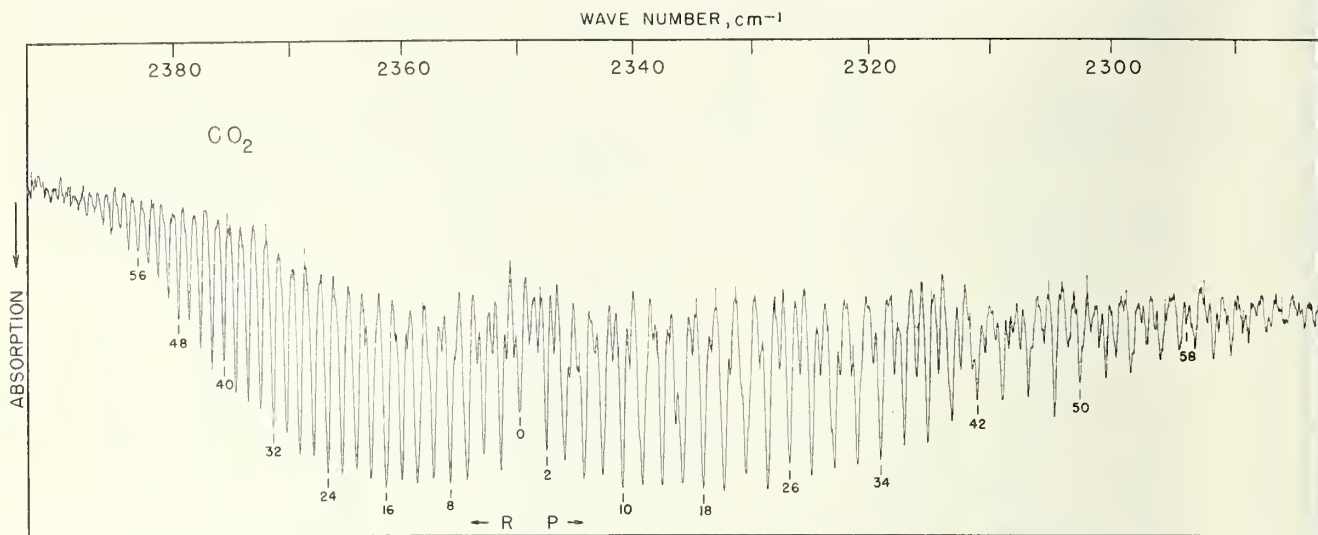


FIGURE 7-B. The ν_3 fundamental of $\text{C}^{12}\text{O}_2^{16}$ recorded in the third order of a 70 lines/mm grating with a small grating instrument. The spectrometer housing was purged of atmospheric CO_2 with dry nitrogen and the spectrum recorded with 30-mm CO_2 in a 10-cm cell. Spectral slit width about 0.25 cm^{-1} .

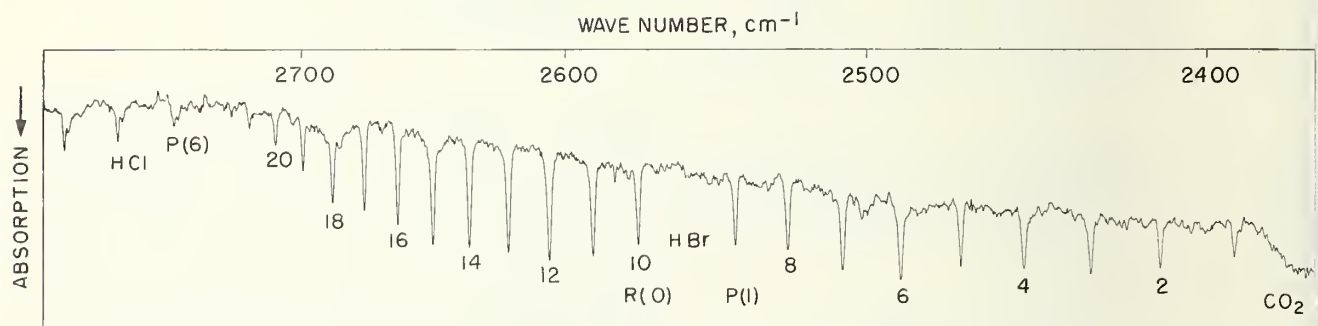


FIGURE 8-A. Absorption band of HBr recorded in the second order of a 5,000 lines/in. grating with 40-cm pressure and 5-cm path. Spectral slit width about 0.8 cm^{-1} . The CO_2 band just appears at the low frequency end and the HCl band at the high frequency side. HCl was present in the HBr as an impurity.

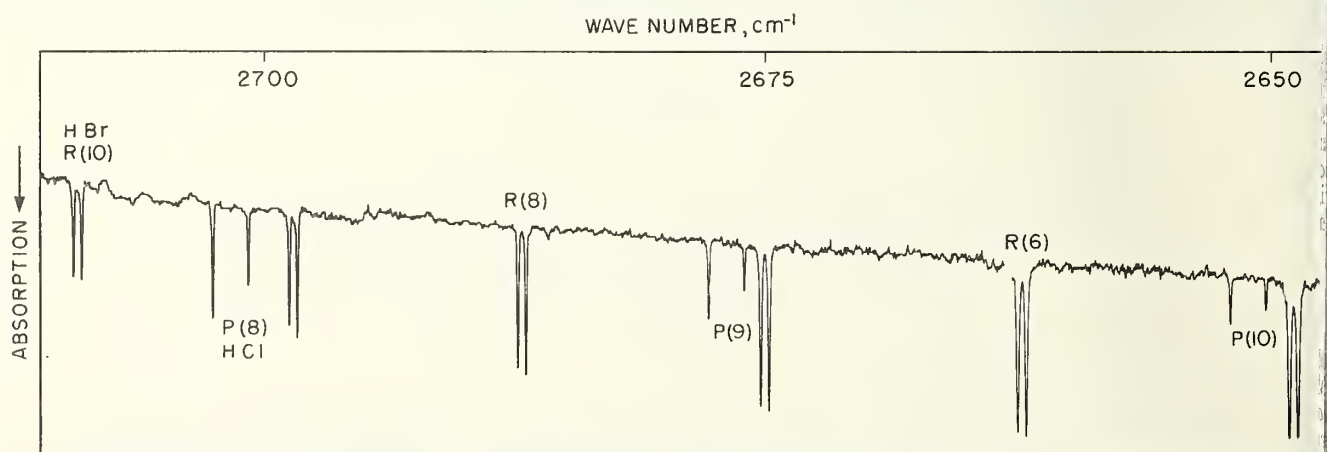


FIGURE 8-B. A section of the $\text{HBr}^{79, 81}$ bands with $\text{HCl}^{35, 37}$ overlapping. Recorded with a 10,000 lines/in. grating singly passed with 2.5-mm pressure of each acid in a 6-m cell. Spectral slit width about 0.06 cm^{-1} .

TABLE 7-B. Absorption lines of ν_3 fundamental of $\text{C}^{12}\text{O}_2^{16}$ from 2,280 cm^{-1} to 2,390 cm^{-1}

Line number	This work ν cm^{-1} (vac.) observed	Previous work this laboratory ν cm^{-1} (vac.) observed	Line number	This work ν cm^{-1} (vac.) observed	Previous work this laboratory ν cm^{-1} (vac.) observed
P 68	2,282.21		R 48		2,379.80
66			50		80.74
64	86.93		52		81.65
62	89.23		54		82.51
60			56	2,383.39	83.38
58	93.81	2,293.81	58	84.22	84.21
56	96.03	96.03	60	85.01	85.01
54	98.30		62	85.80	85.79
52	2,300.50		64	86.55	86.55
50		2,302.70	66		87.26
48		04.84	68		87.97
46		06.96	70		88.64
			72		89.32
			74		89.91
			76		90.49
R 30		2,370.36			
32		71.48			
34		72.65	78		91.10
36		73.71	80		91.61
38		74.79	82		92.16
			84		
40		75.83	86		93.09
42		76.87			
44		77.88	88		93.55
46		78.86	90		93.96

Calculated values for lines near band center

P 44	2,309.05	R 0	2,349.97
42	11.13	2	51.50
40	13.19	4	53.01
38	15.22	6	54.49
36	17.23	8	55.95
34	19.21	10	57.38
32	21.17	12	58.78
30	23.11	14	60.16
28	25.02	16	61.52
26	26.91	18	62.86
24	28.77	20	64.16
22	30.60	22	65.44
20	32.41	24	66.70
18	34.20	26	67.93
16	35.97	28	69.13
14	37.71		
12	39.43		
10	41.12		
8	42.78		
6	44.42		
4	46.04		
2	47.63		

* E. K. Plyler and L. R. Blaine, unpublished work.

Observed and calculated values should be good to about $\pm 0.02\text{-cm}^{-1}$ absolute. Since the band consists of a collection of no less than four overlapped bands, results are subject to being extremely resolution sensitive and workers should not use lines exhibiting pronounced overlap. (The R branch is comparatively free of such difficulties.)

5.9. HBr Fundamental

As shown in figures 8-A and 8-B, this band was measured under considerably different resolution. With the conditions describing figure 8-A, there was no evidence to the effect that the components arising from HBr^{79} and HBr^{81} were being resolved out. This was done intentionally to see whether, when measured as a single peak, the frequency agreed with the average determined for each component under

resolution approaching 0.05 cm^{-1} . The low resolution single-peak frequency agreed with the high resolution average value to within 0.05 cm^{-1} on the average (See table 8). This relatively good agreement does indicate that the high resolution results are correct in the absolute sense and that apart from greater inability to determine the center of the single

TABLE 8. Absorption lines of HBr^{79} and HBr^{81} together with single unresolved peaks at lower resolution (2,390–2,750 cm^{-1})

Serial number	This work high resolution isotopic components ν cm^{-1} (vac.) observed	High resolution average	This work low resolution single peak ν cm^{-1} (vac.) observed
1	Br^{81} 2,392.61		
	Br^{79} 92.94	2,392.78	
	Br^{81} 2,412.73		
2		2,412.89	2,412.93
	Br^{79} 13.06		
	Br^{81} 32.43		
3		32.60	32.65
	Br^{79} 32.77		
	Br^{81} 51.73		
4		51.91	51.94
	Br^{79} 52.08		
	Br^{81} 70.61		
5		70.79	70.82
	Br^{79} 70.97		
	Br^{81} 89.08		
6		89.26	89.30
	Br^{79} 89.43		
	Br^{81} 2,507.11	2,507.30	2,507.24
7			
	Br^{79} 07.48		
	Br^{81} 24.71		
8		24.90	24.83
	Br^{79} 25.08		
	Br^{81} 41.87		
9		42.06	41.99
	Br^{79} 42.25		
	Br^{81} 74.80		
10		74.99	74.98
	Br^{79} 75.19		
	Br^{81} 90.56		
11		90.76	90.67
	Br^{79} 90.95		
	Br^{81} 2,605.82	2,606.02	2,605.95
12			
	Br^{79} 06.22		
	Br^{81} 20.63		
13		20.83	20.81
	Br^{79} 21.03		
	Br^{81} 34.92		
14		35.13	35.03
	Br^{79} 35.33		
	Br^{81} 48.71		
15		48.92	48.85
	Br^{79} 49.13		
	Br^{81} 61.99		
16		62.19	62.13
	Br^{79} 62.39		
	Br^{81} 74.76		
17		74.97	
	Br^{79} 75.19		
	Br^{81} 87.00		
18		87.20	
	Br^{79} 87.41		
	Br^{81} 98.68		
19		98.90	
	Br^{79} 99.11		
	Br^{81} 2,709.86		
20		2,710.07	
	Br^{79} 10.29		
	Br^{81} 20.48		
21		20.68	
	Br^{79} 20.89		
	Br^{81} 30.51		
22		30.73	
	Br^{79} 30.95		
	Br^{81} 40.02		
23		40.24	
	Br^{79} 40.46		
	Br^{81} 48.93		
24		49.16	
	Br^{79} 49.39		

peak (near 1-cm^{-1} half-width), its frequency is given well enough by the component average. In table 8, the high resolution average of components is the recommended value for single peak use. Calculated values were also determined for the high resolution results and the values given in the first column of table 8 are believed to be accurate to within $\pm 0.02\text{-cm}^{-1}$ absolute.

5.10. HCl Fundamental

The spectrum illustrated in figure 9 was recorded under low resolution and the entire band shown in this way for the sake of compression. Figure 8-B shows 3 lines of the band under high resolution. The band was measured on both instruments in this laboratory and results are compared with values reported by Mills, Thompson, and Williams [28] (see table 9). Molecular constants were obtained from the high resolution observations and calculated line frequencies agree well with the observed. In general, the high resolution results of this work fall between the low resolution values and those of Mills, Thompson, and Williams. The high resolution work does not, however, represent precision measurement, since the lines were measured at medium-fast scan in order to appropriately cover this extremely wide band in reasonable time. The observed values given in the table for the high resolution work are to be preferred and represent the best possible set. These values should be good to about $\pm 0.02\text{-cm}^{-1}$ absolute. (Future precision measurements are contemplated for this band.)

5.11. Methane, ν_3 Band

The R branch of this band and some of the lower- J lines of the P branch are fairly suitable for providing calibration points in this region. However, care should be exercised to the extent of staying within the bounds of the resolution illustrated in figure 10.

TABLE 9. Absorption lines of HCl from 2,650 to 3,050 cm^{-1}

Serial number	This work high resolution ν cm^{-1} (vac.) observed	This work high resolution ν cm^{-1} (vac.) calculated	This work low resolution ν cm^{-1} (vac.) observed	M., T., and W. ν cm^{-1} (vac.) observed
HCl ³⁵				
0.....	2,651.98	2,651.98	-----	.92
1.....	77.74	.75	.86	.74
2.....	2,703.02	2,703.02	.03	2.94
3.....	27.79	.79	.76	.73
4.....	52.05	.05	.15	.03
5.....	75.77	.77	.85	.79
6.....	98.95	.95	.96	9.04
7.....	2,821.58	2,821.57	.56	.55
8.....	43.63	.63	.60	.66
9.....	65.10	.10	.14	.11
10.....	2,906.25	2,906.25	.24	.22
11.....	25.91	.90	.89	.99
12.....	44.92	.92	-----	.99
13.....	63.30	.30	.20	.33
14.....	81.02	.02	-----	.03
15.....	98.07	.07	-----	.06
16.....	3,014.44	3,014.44	-----	.51
17.....	30.10	.11	.12	.11
18.....	45.07	.08	.02	.11
HCl ³⁷				
0.....	2,650.23	2,650.24	-----	.11
1.....	75.96	.96	-----	.99
2.....	2,701.20	2,701.19	.28	.11
3.....	25.93	.93	.95	.99
4.....	50.14	.14	-----	.11
5.....	73.84	.83	.89	.88
6.....	96.98	.98	-----	7.04
7.....	2,819.57	2,819.57	-----	.55
8.....	41.59	.59	-----	.55
9.....	63.02	.03	-----	.03
10.....	2,904.12	2,904.12	.14	.06
11.....	23.74	.74	.79	.77
12.....	42.74	.73	.66	.77
13.....	61.08	.08	.06	.11
14.....	78.77	.77	-----	.88
15.....	95.79	.79	-----	.77
16.....	3,012.15	3,012.14	.14	.22
17.....	27.80	.79	.72	.88
18.....	42.74	.74	.68	.88

^a Mills, Thompson, and Williams [28].

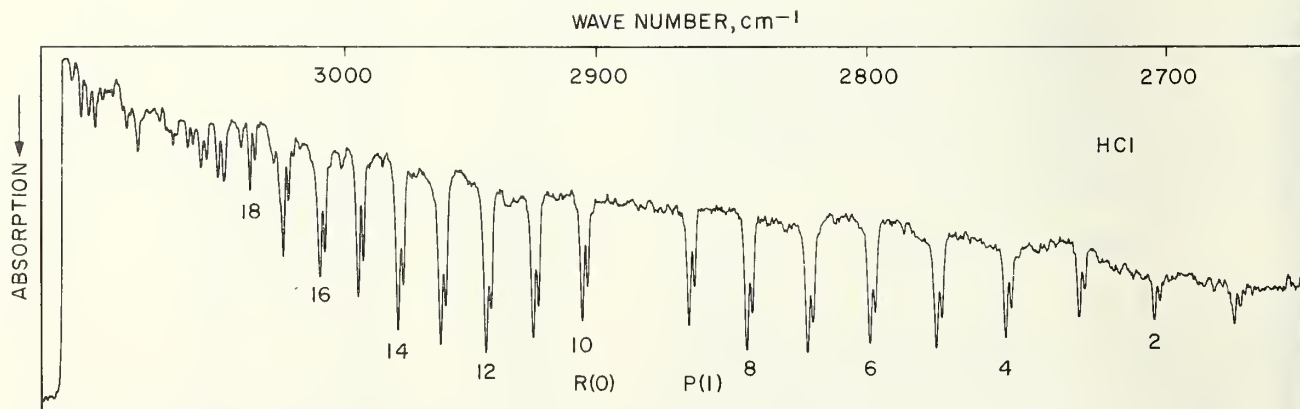


FIGURE 9. Absorption band of HCl recorded in the second order of a 5,000 lines/in. grating with 20-cm pressure and 5-cm path. Spectral slit width about 1.0 cm^{-1} . Weak atmospheric water lines of the $2\nu_2$ band begin to appear at the high frequency end.

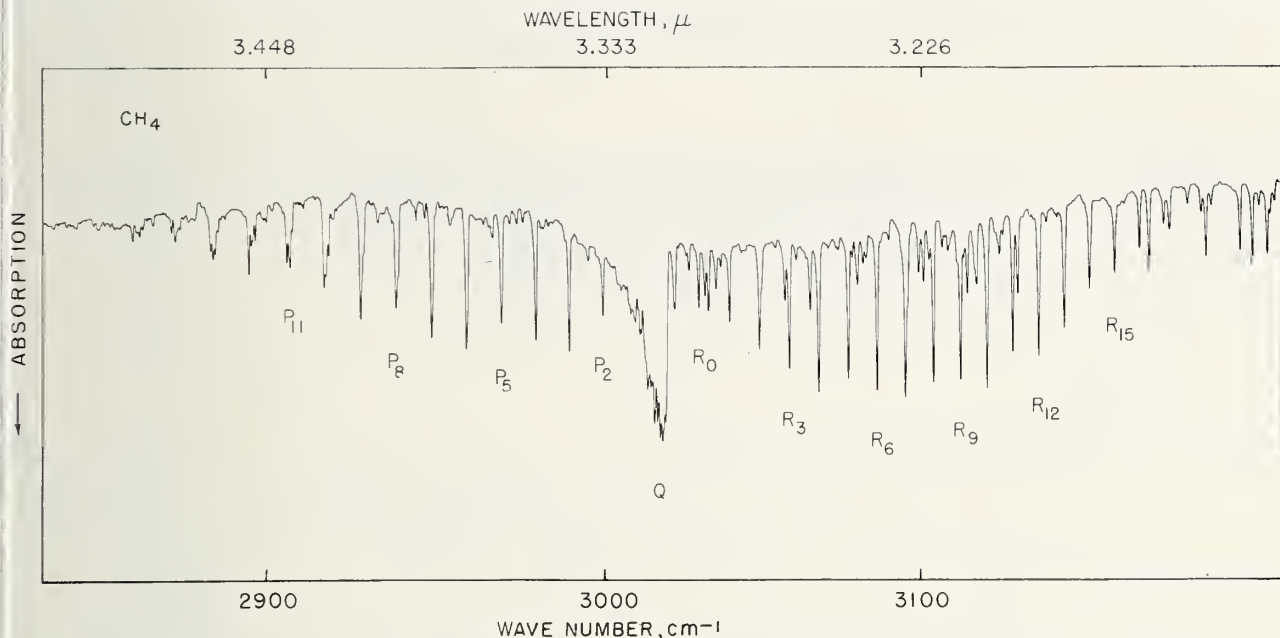


FIGURE 10. The ν_2 fundamental of methane recorded with a 7,500 lines/in. grating with 10-cm pressure and 5-cm path. Spectral slit width about 0.9 cm^{-1} . certain weak lines occurring between methane lines are part of the $2\nu_2$ band of atmospheric water vapor.

Under higher resolution the lines begin to break up, P_4 , for example, shows four components within 0.37 cm^{-1} and frequency allocation becomes difficult. The values are listed in table 10 and strongest components should be used where indicated.

5.12. Acetylene Bands Near 3,300 cm^{-1}

The spectrogram of figure 11 gives a rather interesting comparison of lines and peaks under considerably differing resolution. The scale on the lower

panel, though close to that of the upper one differs somewhat and is indicated by the tie lines. The values listed in table 11 indicate the rather remarkable feature that even under considerably lower resolution single or symmetrical lines can still be accurately measured. The high resolution measurements were made with fringes and the grating circle was used for the lower resolution measurements. In two cases (lines 6 and 7; 20 and 21), two closely spaced and nearly equal intensity components were measured as a single peak and this value compared with the average of the two components. As in the case of HBr, the agreement is quite satisfactory. The results of this work are compared with values reported by Christensen, Eaton, Green, and Thompson (see ref. [23]).

TABLE 10. Absorption lines of methane from 2,900 to 3,170 cm^{-1}

Line number	Plyler, Blaine, and Nowak ^a ν cm^{-1} (vac.) observed	Line number	Plyler, Blaine, and Nowak ^a ν cm^{-1} (vac.) observed
P 12	^b 2,895.18	R 0	3,028.84
11	^b 2,906.72	1	38.58
10	^b 16.36	2	48.25
9	26.86	3	57.79
8	37.34	4	67.30
7	47.92	5	76.74
6	58.20	6	86.02
5	68.67	7	95.22
4	79.00	8	3,104.36
3	88.27	9	13.42
2	99.10	10	22.46
		11	31.39
		12	40.20
		13	48.95
		14	57.61
		15	66.20

^a Plyler, Blaine, and Nowak [11].
^b Frequency of strongest component.

5.13. Water and Carbon Dioxide Bands Near 3,700 cm^{-1}

The spectrogram (fig. 12-A), illustrating the atmospheric absorption in this region, was recorded with the low resolution instrument so that results would approximate those attainable with small grating instruments. The indicated lines were measured under these conditions and in table 12-A the results are compared with the high resolution and high precision work of Plyler and Tidwell [29]. The agreement is satisfactory and indicates that even with lower resolution, good measurements in the order of 1 part in 100,000 can still be made. The higher resolution numbers are the recommended ones and if more frequent calibrating points are required, workers should make use of reference [29].

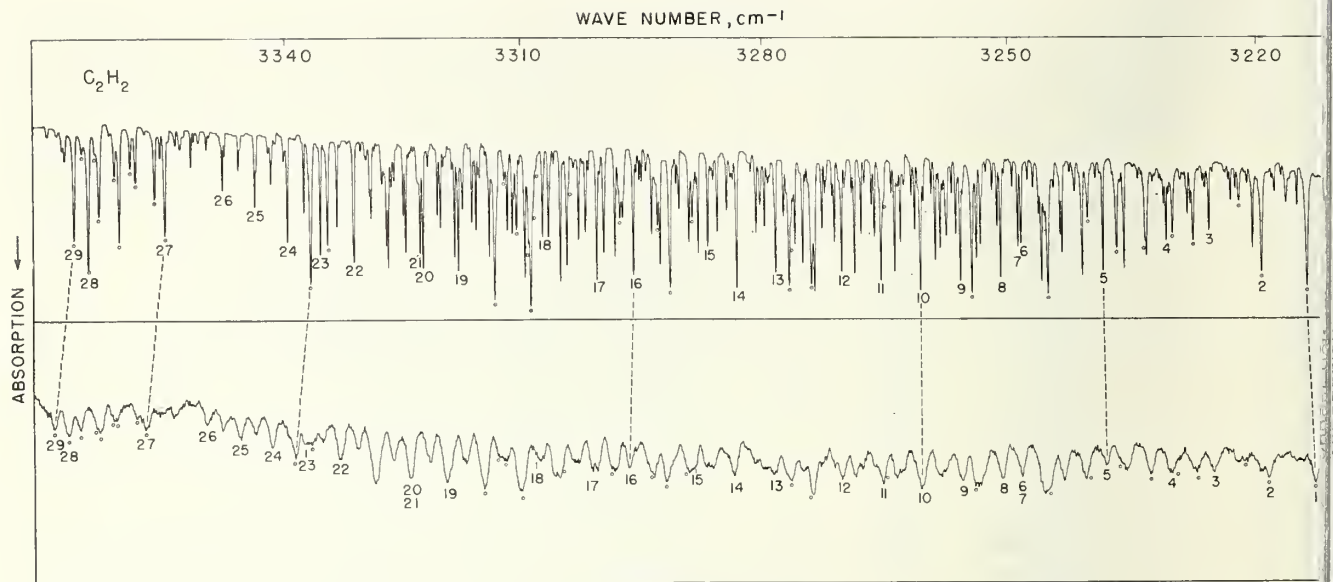


FIGURE 11. The two absorption bands of acetylene near $3,300\text{ cm}^{-1}$ compared under high and lower resolution.

The upper spectrogram was recorded with a 10,000 lines/in. grating singly passed with 1.5-cm pressure and 5-cm path. The lower spectrogram was recorded in the second order of a 5,000 lines/in. grating with 4-cm pressure and 5-cm path. Spectral slit widths about 0.10 and 0.8 cm^{-1} , respectively. Atmospheric water lines of the $2\nu_2$ band are denoted by open circles.

TABLE 11. Absorption bands of acetylene (2 bands) from $3,200$ to $3,380\text{ cm}^{-1}$

Serial number	This work medium-high resolution $\nu\text{ cm}^{-1}$ (vac.) observed	This work low resolution $\nu\text{ cm}^{-1}$ (vac.) observed	C., E., G., and T. ^b medium resolution $\nu\text{ cm}^{-1}$ (vac.) observed
2	3,219.42 (H ₂ O)	-----	-----
3	25.63	-----	.64
4	30.72	-----	.72
5	38.31	.44	.29
6	48.19 ^a 48.38	48.41	.34 ^a 48.40
7	48.56	-----	.47
8	50.71	.82 (slightly blended)	.65
9	55.59	-----	.56
10	60.46	.60 (slightly blended)	.40
11	65.29	.32	.26
12	70.10	-----	.04
13	78.22	-----	.20
14	83.04	.14	2.93
15	86.63	-----	.48
16	95.88	.80	.83
17	3,300.46	-----	.35
18	07.27	-----	.14
19	17.92	-----	.99
20	22.41 ^a 22.59	22.62	22.44
21	22.77	-----	-----
22	31.29	.31	.18
23	35.59	-----	.49
24	39.83	.98	.72
25	44.08	.01 (slightly blended)	3.93
26	48.23	.21	.08
27	55.74 (H ₂ O)	-----	-----
28	65.78 (H ₂ O)	.86	-----
29	67.67 (H ₂ O)	-----	-----

^a Average of two components of nearly equal intensity.

^b Christensen, Eaton, Green, and Thompson [23].

5.14. CO₂, O₂1, and 101 Bands

Plyler and Tidwell (see ref. [29]) report the precise measurement of many of these lines. Certain others which could not be measured due to overlapping water lines, are not listed in table 12-B. Most of these lines are good to about $\pm 0.02\text{ cm}^{-1}$. The two bands are illustrated in figure 12-B as recorded with a nitrogen-purged small grating instrument with CO₂ in a cell. (The spectrogram was recorded by Dr. Norman Jones, National Research Council Ottawa, Canada.)

5.15. C₂H₂, $\nu_1 + \nu_5$ Band

From the end of the P branch of the CO harmonic to the beginning of the ν_3 water vapor band there is a gap of about 100 cm^{-1} . There is a band of acetylene of medium intensity that falls in this region ($4,039$ to $4,130\text{ cm}^{-1}$). This band is overlapped by four weaker bands and when measured with low pressure and high resolution many lines are observed [30]. When a pressure of 1 atm is used in a 10-cm cell, the smaller bands are not observed and the P and R branches of the band stand out clearly. A number of the strong lines were measured under both high and low pressures and the values agree closely. The numbers listed in table 13 are the results of the low pressure measurements. The spectrum is shown in figure 13.

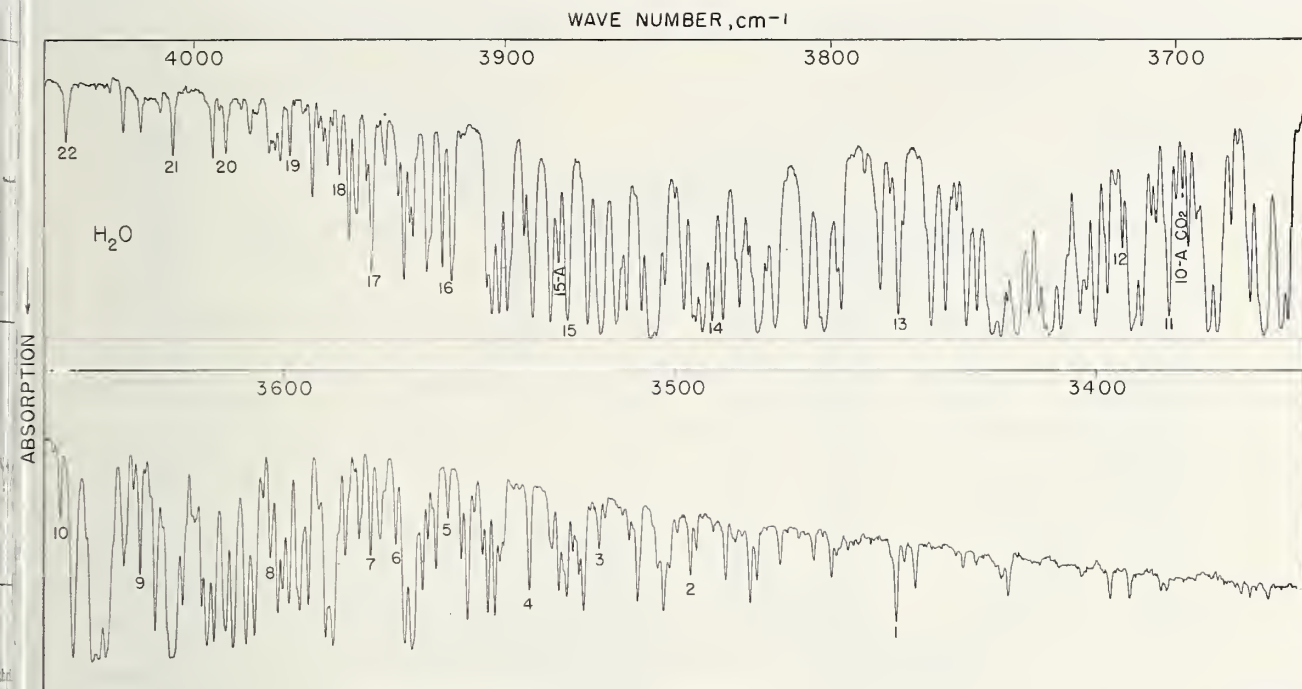


FIGURE 12-A. Atmospheric absorption bands of H_2O and CO_2 in the $3,700\text{-cm}^{-1}$ region recorded under intermediate resolution in the second order of a $5,000\text{ lines/in.}$ grating.

The path was 7 m with 48 percent humidity at 23°C . Spectral slit width about 0.7 cm^{-1} .

TABLE 12-A. Absorption lines of water from $3,400$ to $4,000\text{ cm}^{-1}$

Line serial number	High resolution Plyler and Tidwell ^a $\nu\text{ cm}^{-1}$ (vac.) observed	Intermediate resolution this work $\nu\text{ cm}^{-1}$ (vac.) observed
1	3,397.20	
2	3,447.20 (7.03)	3,447.21
3	96.63	96.62
4	3,518.97	3,519.05
5	(2 components)	36.44 avg
		57.21
6	70.54	70.48
7	76.89	
	77.06 avg	77.02 avg
(8)	77.23	
9	3,603.08	3,602.98 (complex)
10	38.15	38.15
	59.94	59.94
10-A (CO_2)	98.00	98.08
11		3,701.90
12	3,714.81	3,714.82
13		79.38
14		3,835.06
15		80.52
15-A	3,883.26	83.32
16	3,920.10	3,920.28
17		42.86
18	53.11	53.22
19	69.15	69.16
20	90.72	90.74
21	4,008.59	4,008.59
22	44.90	

^a Plyler and Tidwell [29].

TABLE 12-B. Some precisely measured CO_2 lines of the 021 and 101 bands at $3,609$ and $3,716\text{ cm}^{-1}$

Line number	Plyler and Tidwell ^a $\nu\text{ cm}^{-1}$ (vac.) observed	Line number	Plyler and Tidwell ^a $\nu\text{ cm}^{-1}$ (vac.) observed
021 Band			
P 38	3,579.34	R 2	(3,615.25)
36	81.31	10	(21.17)
32	85.21	12	22.50
26	90.78	14	23.93
24	92.65	16	25.27
22	94.42	26	31.85
20	(96.22)	40	40.00
16	99.74		
14	3,601.40		
10	04.81		
8	06.48		
6	08.07		
101 Band			
P 36	3,682.78	R 6	3,720.09
32	86.74	10	22.90
26	92.46	12	24.35
24	94.34	14	(25.72)
20	98.00	18	28.42
18	99.79	20	29.73
14	3,703.29	22	31.01
12	05.02	26	33.48
10	06.70		
8	08.38		

^a Plyler and Tidwell [29].

Values in parentheses indicate lines which may be overlapped by water lines.

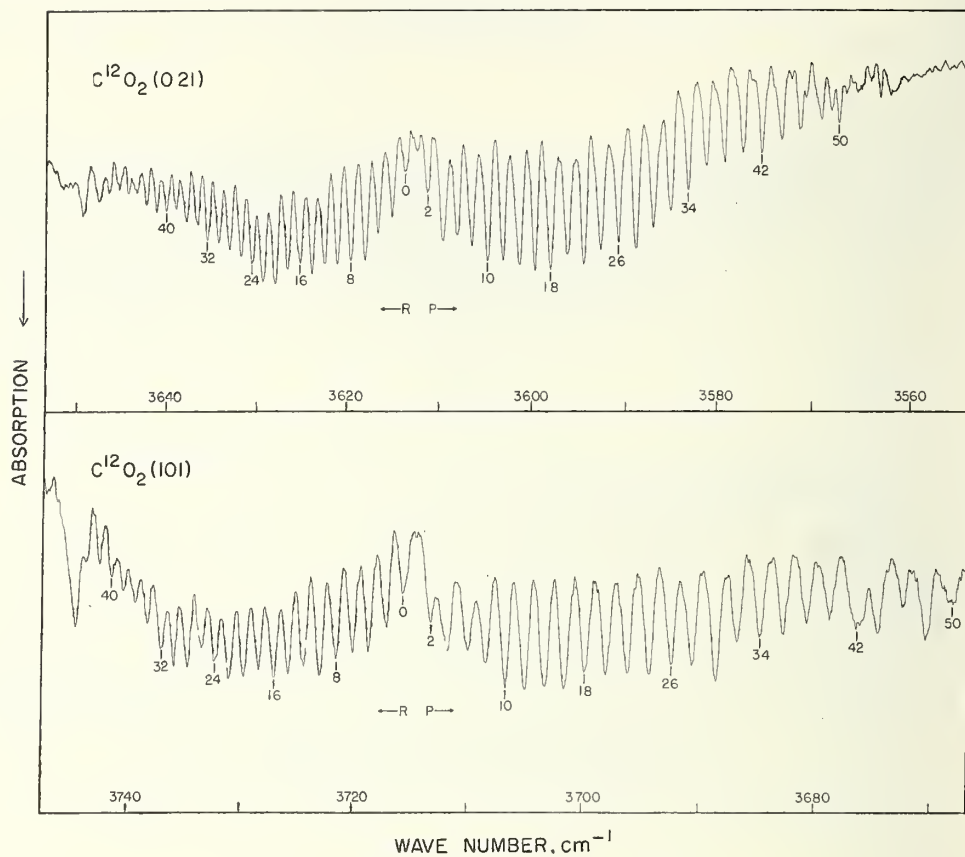


FIGURE 12-B. The 021 and 101 bands of CO_2 recorded with a purged small grating instrument. The CO_2 was contained in a 10-cm cell at 25-cm pressure for both bands. Spectral slit width about 0.30 cm^{-1} .

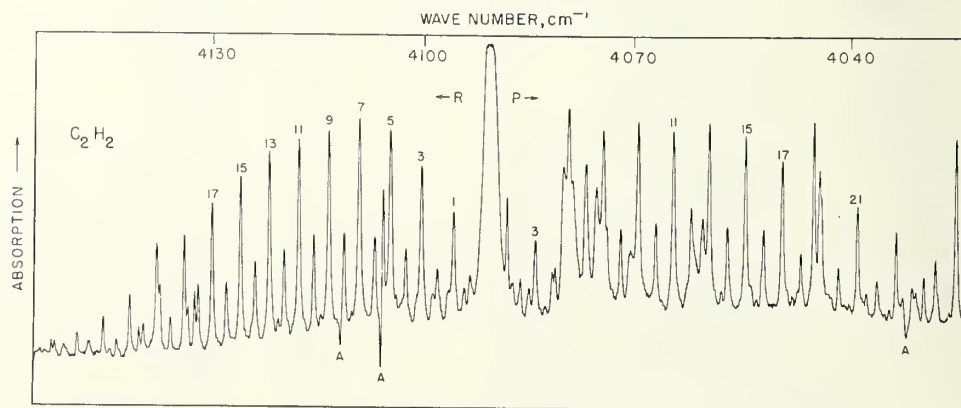


FIGURE 13. The $\nu_1 + \nu_5$ band of acetylene recorded with a 15,000 lines/in. grating singly passed with 1-atm pressure and 10-cm path. Spectral slit width about 0.08 cm^{-1} .

TABLE 13. Absorption lines of acetylene from 4,040 to 4,130 cm^{-1}

Line number	Previous work this laboratory $\nu \text{ cm}^{-1}$ (vac.) observed	Line number	Previous work this laboratory $\nu \text{ cm}^{-1}$ (vac.) observed
P 3	4,084.14	R 17	4,130.10
11	64.58	15	26.91
15	54.52	13	22.63
17	49.36	11	18.30
21	38.95	9	13.94
		7	69.47
		5	64.98
		3	4,100.47
		1	4,095.84

5.16. CO Harmonic Band

The CO harmonic band at 2.34μ has been measured very accurately by Rank and his colleagues (see ref. [14]) and also by Plyler, Allen, and Tidwell (see ref. [15]). This band is one of the few which have been measured in the infrared to such a precision that the reported frequencies are accurate to a few thousandths of a cm^{-1} . This spectrum was measured with a 60-cm cell and 20-cm pressure, but a 10-cm cell with 50-cm pressure is sufficient for observing forty lines of this band. The spectrum is shown in figure 14 and the frequencies are listed in table 14.

TABLE 14. Absorption lines of the 2-0 harmonic band of CO from 4,100 to 4,340 cm^{-1}

Line number	Plyler, Allen, and Tidwell $\nu \text{ cm}^{-1}$ (vac.) observed	Rank et al. ^b $\nu \text{ cm}^{-1}$ (vac.) observed	Line number	Plyler, Allen, and Tidwell $\nu \text{ cm}^{-1}$ (vac.) observed	Rank et al. ^b $\nu \text{ cm}^{-1}$ (vac.) observed
P 27	4,132.19		R 0	4,263.842	.838
26	37.79	.770	1	67.548	.542
25	43.33		2	71.182	.179
24	48.817		3	74.750	.743
23	54.234		4	78.235	.234
22	59.564		5	81.655	.661
21	64.852		6	85.013	.010
20	70.066	.058	7	88.298	.290
19	75.212	.204	8	91.512	.500
18	80.286	.285	9	94.639	
17	85.302	.298	10	97.703	
16	90.234	.242	11	4,300.712	
15	95.120		12	103.614	
14	99.931		13	106.482	
13	4,204.673		14	109.262	.257
12	109.356		15	111.969	.962
11	113.962		16	114.606	.697
10	118.504		17	117.173	.161
9	122.974	.954	18	119.665	.650
8	127.371		19	122.085	.065
7	131.694	.685	20	124.425	
6	135.952	.949	21	126.699	
5	140.150		22	128.878	
4	144.278	.267	23	131.022	
3	148.330		24	133.057	.054
2	152.308	.307	25		4,335.030
1	156.226		26		36.934
			27		38.763
			28		40.517
			29		42.202

^a Plyler, Allen, and Tidwell [15].

^b Rank et al. [14].

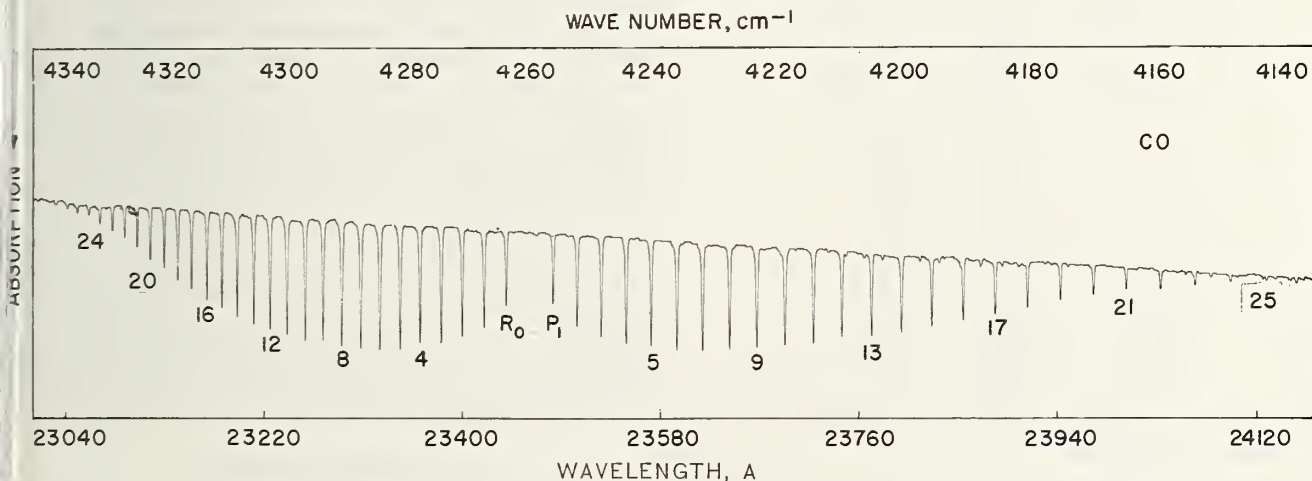


FIGURE 14. The 2-0 band of CO recorded with a 15,000 lines/in. grating with 20-cm pressure and 60-cm path. Spectral slit width about 0.15 cm^{-1} .

5.17. N_2O , $2\nu_1$ Band and Hot Band

The $2\nu_1$ band of N_2O has been measured in the region from 2,520 to 2,580 cm^{-1} and the results are shown in figure 15 and table 15. Thompson and Williams [31] had previously measured this band and their values are used to compare with the results obtained in this work. The lines which have been measured are noted by a dot on the spectrogram.

There is an overlapping structure of weak lines and only those lines were measured which appeared in the open. This band can be resolved by a small grating instrument if a photoconducting cell is used as the detector and could be used as an alternate for HBr in this region. Also there are several regions where lines are closely grouped and the band can be used to check instrumental performance and resolution. The measurements of Thompson and Williams agree, on the average, to within $\pm 0.04 \text{ cm}^{-1}$ of the

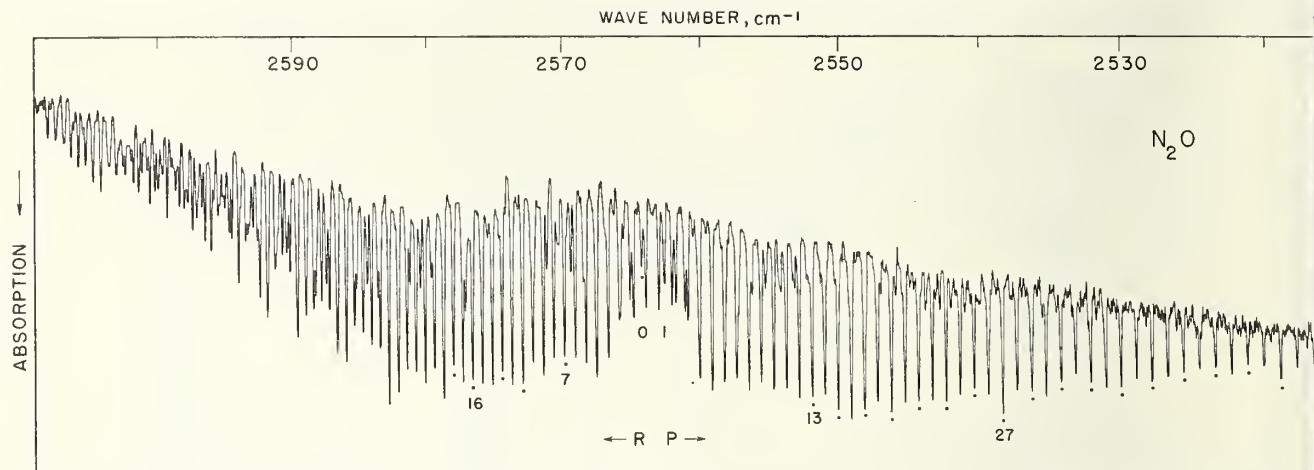


FIGURE 15. The $2\nu_1$ band (2564 cm^{-1}) of N_2O together with the hot band ($2\nu_1 + \nu_2 - \nu_2$, 2577 cm^{-1}) recorded with a 10,000 lines/in grating with 2-mm pressure and 6-m path.

Spectral slit width about 0.08 cm^{-1} . The dots denote the measured and tabulated lines.

TABLE 15. Absorption lines of N_2O from $2,520$ to $2,580\text{ cm}^{-1}$

J	This work $\nu\text{ cm}^{-1}$ (vac.) observed	Thompson and Williams ^a $\nu\text{ cm}^{-1}$ (vac.) obs. laboratory
$P\ 45$	2,519.01	.05
43	21.27	.29
41	23.50	.52
39	25.71	.72
37	27.87	.88
35	30.03	.03
33	32.15	.17
31	34.25	.27
29	36.31	.35
27	38.37	.41
25	40.38	.42
23	42.38	.42
21	44.34	.38
19	46.27	.32
17	48.19	.23
15	50.07	.13
13	51.92	2.01 (1.97 calc.)
$R\ 0$	2,564.18	.24
7	69.82	.86
11	72.87	.94
13	74.38	.45
16	76.56	.59
18	77.99	8.04

^a Thompson and Williams [31].

values in this work. There is a small shift in the direction of lower frequency of all the values of the present measurements. An average of the two sets of values would probably be correct to $\pm 0.03\text{ cm}^{-1}$, which should be entirely adequate for calibrating medium resolution instruments.

5.18. NH_3 , ν_4 Fundamental

This band is being included as an alternate to the $6\text{-}\mu$ water band and should prove of some use to workers who wish to flush their instruments or use double-beam operation to study samples contained in cells. Dr. W. S. Benedict, of the Johns Hopkins

University, has picked out of the band (in accordance with the resolution illustrated in fig. 16) some 1 single or not-too-complex absorption peaks and has determined the best possible frequencies from the higher resolution results of Garing and Nielsen (see ref. [24]) and unpublished results from the National Bureau of Standards Laboratory. The results of these two works agree to within about $\pm 0.02\text{ cm}^{-1}$. The frequency assigned to certain absorption peak which appear single in figure 16 but which actually consist of several components is, of course, no longer applicable if the peak is broken up into its components under slightly higher resolution. (The letter S in figure 16 indicates a single line.) No table accompanies this spectrogram but instead the acceptable values which are probably good to $\pm 0.02\text{ cm}^{-1}$ for single lines and off by as much as $\pm 0.2\text{ cm}^{-1}$ for some complex lines, have been printed on the illustration. For calibration purposes, the ν_1 water lines (see table 5) are considerably better than the lines of this band. (The spectrogram was recorded by Dr. Norman Jones, National Research Council, Ottawa, Canada.)

6. Polystyrene Film

In 1950 Plyler and Peters (see ref. [7]) measured the infrared absorption spectrum of polystyrene on a grating instrument and certain bands were suggested for use in calibrating prism instruments. Since that time, films of polystyrene have been widely used in many laboratories and it has been found very useful in checking the calibration of an instrument in certain regions to ascertain if there are any changes in the reading of the wavelength or frequency scale of the instrument. There is a question as to the suitability of polystyrene for a calibrating material as it is not completely stable and has a different absorption spectrum when it

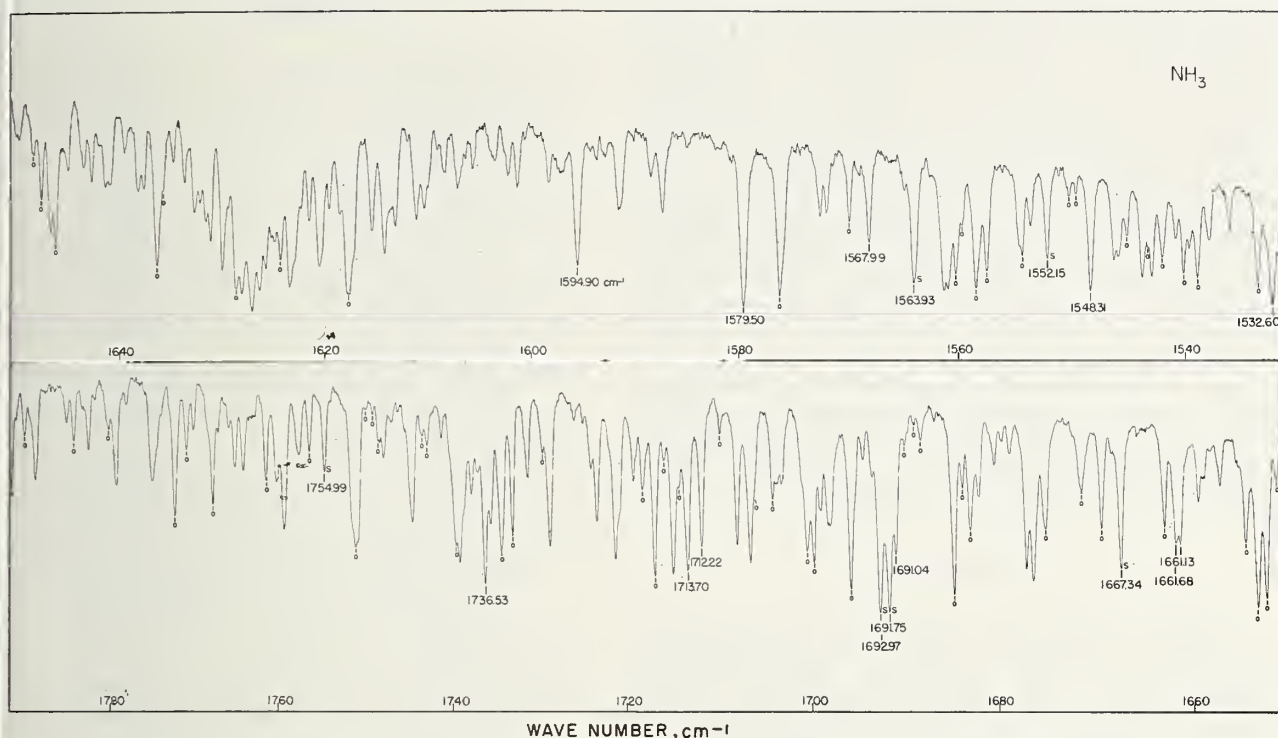


FIGURE 16. The ν_4 band of NH_3 at 1628 cm^{-1} recorded with a nitrogen-purged small grating instrument. Certain strong lines of the ν_2 water band still appear. A gas pressure of 7.5 cm in a 10-cm cell was used. Spectral slit width about 0.50 cm^{-1} .

ges. Also different batches of the material may show differences in absorption. The variation in the absorption spectrum of different films can easily be demonstrated, but the strong bands are not appreciably changed in wavelength by age or the origin of the film. In this work, we checked a film which had been made ten years ago and it showed no appreciable shifts in the absorption bands. Eight bands from 6 to 14.4μ have been remeasured and the results are compared with the previous measurements of 1950 and the additional measurements of Plyler, Blaine, and Nowak (see ref. [11]) in 1957. The spectrum is shown in figure 17 and the wavelengths and wave numbers in vacuum are listed in table 16. When the faces of the film are parallel, interference fringes appear but these usually occur

TABLE 16. Polystyrene absorption bands

Previous measurement wavelength (air) μ	New measurement this work wavelength (air)	This work cm^{-1} (vac.)
3.3026		
3.422		
3.507		
5.138		
5.343		
5.549		
6.238	6.2427	1,601.45
	6.3151	1,583.08
6.692		
	8.4615	1,181.50
8.662	8.6626	1,154.08
	9.3524	1,068.96
9.724	9.7226	1,028.28
11.035	11.028	906.50
	14.316	698.33

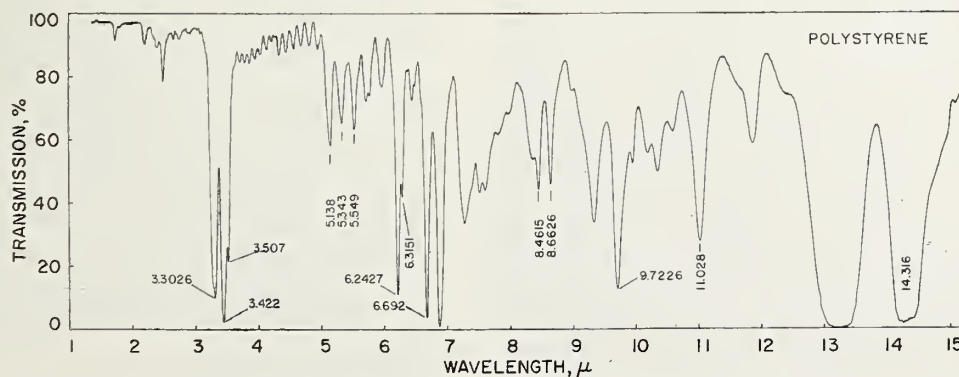


FIGURE 17. Infrared absorption spectrum, from 2 to 15μ , of a $50\text{-}\mu$ film of polystyrene recorded with a rock-salt prism instrument.

between 4 and 6 μ for a 50- μ film and do not change the position of the bands beyond 6 μ . The small band at 6.3151 μ , which is on the long wavelength side of the strong band at 6.24 μ , is completely resolved by a low resolution grating instrument and is not overlapped by atmospheric water lines. It should be useful for calibration in this region. The strong band at 14.316 μ was measured with a film of 8- μ thickness and with this film the maximum of absorption could be accurately determined. It is estimated that the bands listed in table 16 are accurate to ± 0.3 cm^{-1} and should be useful in calibrating low resolution instruments, but should not be considered as being of the same order of accuracy as the molecular vapor bands. In measuring the polystyrene bands, the center was determined near the $\frac{3}{4}$ -absorption point for symmetrical bands and reference should be made to this point when making use of the numbers in table 16.

7. Summary

The rather "popular" ammonia band at 3 μ was not used in this work because of its resolution sensitiveness and also because of temperature and pressure effects. For example, there are 12 components in the P 8 "line" extending over 1.5 cm^{-1} . Under low resolution (see ref. [11]) the Q branch, which extends over 5.5 cm^{-1} and consists of hundreds of lines is probably good to 0.5 cm^{-1} .

The 16- μ coverage may be appropriately extended by making use of frequency values reported by Lakshmi, Rao, and Nielsen [32] for N_2O . In this work, we have checked Rao's measurements on the 15- μ CO_2 band and feel that if the same techniques were used on the N_2O measurements, then these numbers may be used. Considering the lower resolution used by the Japanese workers (see ref. [12]) on this band, the agreement with values reported in [32] above is quite good.

At the high frequency end, we have already given reference to the work of Rank and coworkers on HCN (see ref. [16]) and wish to include also the grating work on H_2O vapor at 1.9 μ and on CH_4 at 2.2 μ as given in reference [8].

The calibrating values given in this report should make it easier for infrared spectroscopists to obtain accurate measurements in the region from 2 to 16 μ . As further measurements are carried out in other laboratories, there will be more values for inter-comparison and it should be possible to obtain calculated values for certain bands which would be more accurate than the observed values from any one laboratory. No recommended frequencies representing properly weighted averages of the work of several laboratories have been given, but this may be done at a later date when more data are available. It is hoped that spectroscopists will send new data of this type to the authors for wavelength standards so that it may be incorporated in a future report. It is also requested that any corrections or suggested changes be communicated to the authors.

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WASHINGTON, D.C.

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THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity and Electronics. Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

Heat. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Molecular Kinetics. Free Radicals Research.

Atomic Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics.

Radiation physics. Neutron Physics. Radiation Theory. Radioactivity. X-ray. High Energy Radiation. Nucleonic Instrumentation. Radiological Equipment.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Safety Standards. Heat Transfer. Concreting Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Applications Engineering.

• Office of Basic Instrumentation.

• Office of Weights and Measures.

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionosphere Research. Regular Prediction Services. Sun-Earth Relationships. VHF Research. Radio Warning Services. Airglow and Aurora. Radio Astronomy and Arctic Propagation.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High-Frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Standards. Electronic Calibration Center. Microwave Circuit Standards.

Radio Communication and Systems. Low Frequency and Very Low Frequency Research. High Frequency and Very High Frequency Research. Modulation Systems. Antenna Research. Navigation Systems. Systems Analysis. Field Operations.

